LIMITS TO INTERSTELLAR C_4 AND C_5 TOWARDS ζ OPHIUCHI

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ABSTRACT

We have made a sensitive search for the origin bands in the known electronic transitions of the linear carbon chains C_4 and C_5 at 3789 and 5109 Å towards ζ Oph ($A_V \leq 1$). The incentive was a recent detection of C_3 in this interstellar cloud with a column density of 1.6×10^{12} cm^{-2} plus the availability of laboratory gas phase spectra of C_4 and C_5. Further, some models of diffuse interstellar clouds predict that the abundance of these latter species should be within an order of magnitude of C_3. Despite achieving S/N of 2300 to 2600 per pixel at a resolution of $\sim$110,000, the searches were negative, leading to 3σ upper limits to the column density of $N(C_5) = 2 \times 10^{11}$ cm^{-2} and $N(C_4) = 4 \times 10^{12-13}$ cm^{-2} where these values rely on theoretically calculated oscillator strengths. The implication of these limits are discussed on the choice of molecules for study in future attempts to identify the carriers of the stronger diffuse interstellar bands.

Subject headings: ISM: molecules— C_4, C_5

1. Introduction

Carbon chain molecules are often at the forefront in discussions of the diffuse interstellar bands (DIB) (see Douglas (1977) and Smith et al. (1977)), which are found mainly in the optical part of

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the spectrum (Herbig 1995). They became more appealing candidates with the discovery at mm wavelengths (McCarthy & Thaddeus 2001) of numerous polar carbon chains in dense interstellar clouds. However, only in the past few years have the gas phase electronic spectra of a number of such species (e.g. C_4, C_5, $C_{2n}H$ n=3-6), as well of related cations (e.g. $HC_{2n}H^+$ n=2-4, $HC_{2n}N^+$ n=2-4) and anions (e.g. C_n^- n=3-11) been detected in the laboratory, enabling direct comparison with astronomical data (for example, Motylewski et al. (1999)). In all cases where the comparisons could be made, the results were negative, leading to the conclusion that the column densities of these species are $\leq 10^{12}$ cm^{-2} in diffuse clouds.

However, with the detection of the rotational lines in the electronic transition of C_3 near 4052 Å (Maier et al. 2001), corresponding to total column densities of 1-2$\times 10^{12}$ cm^{-2}, and the prediction of certain models of such diffuse clouds (e.g. Terzieva & Herbst (1998)) that the abundances of C_4 and C_5 are less than a factor of ten smaller than that of C_3, it became appealing to search for these molecules. A disadvantage compared to the electronic spectrum of C_3 is that, according to theoretical predictions, the oscillator strengths of the transitions appear to be smaller. Unfortunately, experimentally determined oscillator strengths are unavailable. These smaller oscillator strengths result in higher abundance limits than was the case for C_3. Apart from the abundances predicted for C_4 and C_5, the detection of both C_3 and C_5 in the infrared by Bernath et al. (1989) in a circumstellar shell provides a guideline. In the latter work the concentration of C_5 proved to be some ten times less than that of C_3.

Here we report an attempt to detect the origin bands of the electronic transitions of C_4 ($^3\Sigma_u^-$ $- ^3\Sigma_g^-$) at 3789 Å and of C_5 ($^1\Pi_u - ^1\Sigma_g^+$) at 5109 Å in absorption towards the reddened star ζ Oph (HD 149757) with the Gecko spectrograph of the Canada-France-Hawaii 3.6 m telescope. There is already one report in the literature of a non-detection of C_5 (Galazutdinov et al. 2001). The present study is an order of magnitude more sensitive. There is no prior attempt reported to detect C_4 in interstellar clouds, but the electronic spectrum in the gas phase was only obtained a year ago (Linnartz et al. 2000).

2. The Observations

The reddened star ζ Oph (HD 149757), was observed on 29 and 30 June 2001 (UT) with the Gecko echellette spectrograph, fiber fed from the Cassegrain focus of the Canada-France-Hawaii 3.6-m telescope (CFHT) (Baudrand & Vitry 2000). This star is bright, having a visual extinction, A_v, near 1 with a rich spectrum of sharp interstellar lines. Crawford (1997) has resolved the interstellar C_2 at 8756 Å into two close velocity components separated by 1.1 km s^{-1} which is hard to resolve at our resolution. The rapidly rotating star, η UMa (HD 120315) was observed as standard.

The detector was the rear illuminated EEV1 CCD (13.5 μm^2 pixels) and the spectral regions were centered at 3789 Å in the 15th order, and at 5109 Å in the 11th order. The 15th order was isolated by the Gecko ultraviolet grism, the 11th by the blue grism. Individual spectra of ζ Oph

were exposed for 15 minutes at 3789 Å and 6 minutes at 5109 Å. The feed fibre was continuously agitated to overcome modal noise (see Baudrand & Walker (2000)). Lines in Th/Ar comparison arc spectra, taken before and after each set of stellar spectra, typically had FWHM of 3 pixels, corresponding to resolutions of $R = 115000$ and 109800 at 3789 and 5109 Å, or 0.0109 and 0.0155 Å pxl^{-1}, respectively. Extensive series of flat-field spectra of a quartz-iodide lamp were recorded for each spectrograph setting and groups of biases were taken several times each night.

Conditions were not ideal to achieve the very high S/N (>4000) which we felt necessary to detect the C_4 and C_5 bands. Only parts of two of the assigned nights were clear and the flat-field spectra displayed an unstable structure typical of modal noise. The stellar spectra did not show the same structure and we were able to demonstrate that the main fiber agitation was working as designed but a misalignment of the fiber feeding the the light of the flat field lamp to the main fiber may have caused the problem. For this reason a combination of flat fields and standard stellar spectra were used in the reduction.

The many biases taken throughout the observing run were averaged to remove the zero-level offset in the spectra for both wavelength regions. For the 5109 Å spectra, obtained after the noise problem with the flat field exposures had been recognized, η UMa was observed at a S/N level substantially higher than ζ Oph. Since the spectrum of the standard star is featureless near 5109 Å its spectrum was used in place of flat field spectra.

Unfortunately, at 3789 Å, weather constraints prevented observations of η UMa at a sufficient S/N level for them to be used directly as flat fields. Instead, we averaged the flat field exposure to remove pixel-to-pixel sensitivity variations in the spectra of both η UMa and ζ Oph. One dimensional spectra of both stars were then extracted in a standard manner. Because of the modal noise in the flat field spectra, each flat field corrected stellar spectrum shows a residual low frequency modal noise pattern. We therefore smoothed the featureless, flat fielded spectrum of η UMa with a 10-point box car filter and then divided the ζ Oph spectrum by this smoothed spectrum to remove the modal noise residuals without seriously degrading the inherently high S/N of the ζ Oph spectrum. For clarity this reduction procedure is illustrated in Figure 1.

Low-order polynomial fits to the positions of the Th/Ar arc spectra were used to calibrate the ζ Oph spectra in wavelength. The spectra were then normalized to the continuum and heliocentric corrections applied. The observations are summarised in Table 1 which lists exposure times and S/N per pixel for each spectral region. The final column gives the radial velocities of the interstellar K I 4044.1 and 4047.2 Å lines as quoted by Maier et al. (2001). These velocities were applied to each spectrum to put the interstellar features on a laboratory scale before making the comparisons discussed in the next section. The comparisons are shown in Figures 2 and 3 where the stellar spectra have been smoothed with a 3-pixel box car filter.

The 3σ detection limits are derived from:

$$W_{max} = 3(wd)^{\frac{1}{2}}(S/N)^{-1}$$

where the 3σ limiting equivalent width, W_{max}, and the FWHM of the feature, w, are both measured in Å, the spectrograph dispersion, d, in Å pixel^{-1}, and S/N is the signal to noise per pixel. We adopted $w = 0.24$ and 0.13 for the 3789 and 5109 Å laboratory features, respectively.

3. Results and Discussion

Our attempt to detect the C_4 3789 Å origin band of the known electronic systems in absorption through the diffuse cloud towards the reddened star ζ Oph was negative. In Figure 2 we compare the stellar spectrum with one from the laboratory (Linnartz et al. 2000) recorded at a temperature of around 50 K. This temperature should be representative for a non-polar molecule in diffuse interstellar clouds; in the case of C_2 (Lambert et al. 1995) and C_3 (Maier et al. 2001), comparable temperatures have been inferred. The laboratory spectrum (which differs from the published one only in that the overlapping C_2 lines have been removed) shows that the rotational lines are lifetime broadened allowing only the lines in the P-branch to be resolved. The intense part of the band to the blue is the R-head and this feature was primarily sought in the astronomical spectrum. The 3σ upper limit for the equivalent width (W_{max}) detection of the R-head is 0.67×10^{-4} Å. The upper limit to the column density N_{max} can then be derived from:

$$N_{max} = 1.13 \times 10^{20} W_{max}/\lambda^2 f \quad cm^{-2}$$

where f is the oscillator strength of the band at wavelength λ in Å.

Though the $^3\Sigma_u^- - {}^3\Sigma_g^-$ electronic transition of C_4 has been observed in the gas phase, the oscillator strength f is not known experimentally. Two values from ab initio calculations are available which, however, differ by an order of magnitude. The first study yielded $f{=}0.003$ (Pacchioni & Koutecky 1988) whereas the second gave f=0.0005 (Mühlhäuser et al. 2000). The values are for the whole band system and thus the f_{0-0} for the 3789 Å band will be reduced by the Franck-Condon factor for this transition. Based on the intensity distribution of the vibrational bands observed in the absorption spectrum measured in a neon matrix (Freivogel et al. 1996), this may be a factor of 5. Thus, taking f_{0-0} in the 0.0001 to 0.001 range leads to $N(C_4) \leq 4 \times 10^{12}$ to 10^{13} cm^{-2}.

Two more recent models of diffuse interstellar clouds (of which the data have been made available to the authors) with characteristics comparable to the one towards ζ Oph (van Dishoeck & Black 1986) yield $N(C_3)/ N(C_4)$ ratios of about 2 (Terzieva & Herbst 1998), and 13 (Turner 2000). The detected total column density of C_3 is 1.6×10^{12} cm^{-2} (Maier et al. 2001). Thus, in view of the uncertainty in the oscillator strength, it is not possible to assess the predictive value of the models.

The situation is similar for C_5. The band system with the 5109 Å origin band shown in Figure 3 was observed first in absorption in a 5 K neon matrix (Forney et al. 1996) and then in the gas phase (Motylewski et al. 1999). It was assigned as the $^1\Pi_u - {}^1\Sigma_g^+$ electronic transition by analogy to the

comet band system of C_3. The rotational structure is only partially resolved due to line widths of 0.7 cm^{-1} (homogeneous broadening due to intramolecular processes). The oscillator strength f_{0-0} = 0.02 was estimated by taking the experimentally known value for C_3 ($f_{0-0} = 0.016$) and scaling this up by the length of the molecule, as simple quantum models such as particle in a box predict.

However, on the basis of recent theoretical calculations, it is proposed that the 5109 Å band system is in fact a forbidden transition, to $^1\Delta_u$ and/or $^1\Sigma_u^-$ states (Hanrath & Peyerimhoff 2001). The oscillator strength could not be calculated because the vibronic effects which lead to its intensity would have to be correctly accounted for.

There is another band system in the neon absorption spectrum with origin band at 4454 Å (unpublished data from the laboratory at Basel), which would then be the $^1\Pi_u$ - $^1\Sigma_g^+$ electronic transition, with calculated oscillator strength of 0.03 (Hanrath & Peyerimhoff 2001); an earlier f value for this transition was 0.037 (Kolbuszewski 1995). A pragmatic approach to the estimation of the oscillator strength for the 5109 Å band is to use the relative intensities of the absorption systems in the 5 K neon matrix. The 4454 Å absorption band system appears about a factor of 5 more intense than the 5109 Å one, implying an f value for the system of around 0.006. The f_{0-0} value for the 5109 Å band will then be reduced further by its Franck-Condon factor, to yield f_{0-0} around 0.001. The lower spectrum in Figure 3 is that recorded towards ζ Oph. The signal-to-noise ratio (2600) is high, leading to a 3σ detection limit of 5×10^{-5} Å. As the laboratory spectrum corresponds to a temperature of around 50 K, about 10 rotational lines comprise the Q-band head. This means that our astronomical measurements had a detection limit for an individual rotational line of $\sim 5 \times 10^{-6}$ Å. For a lower temperature of say, 10 K, there would still be some five lines unresolved within the band to give a 3σ limit per line of $\sim 10^{-5}$ Å.

Our 3σ detetection limit of $\sim 5 \times 10^{-5}$ Å for the band, together with $f_{0-0} = 0.001$, leads to N(C_5) $\leq 2\times10^{11}$ cm^{-2}. Galazutdinov et al. (2001) recently reported a value of N(C_5) $\leq 10^{11}$ cm^{-2}, however the authors were unaware of the spectroscopic problems associated with the oscillator strengths and used a value of f_{0-0} of 0.02. Taking the presently suggested f_{0-0} =0.001 increases their value to N(C_5) $\leq 2\times10^{12}$ cm^{-2}, which is an order of magnitude less sensitive than our results.

3.1. Conclusion

According to the results reported here, N(C_4) $\leq 4\times10^{12}$ to 10^{13} cm^{-2}, and N(C_5) $\leq 2\times10^{11}$ cm^{-2} in the diffuse cloud towards ζ Oph, while N(C_3) = 1.6×10^{12} cm^{-2} from the earlier study (Maier et al. 2001). From these column densities we calculate abundances relative to the total column density of hydrogen (n(H) + 2n(H_2)), 1.3×10^{21} cm^{-2} (from Table 2 of van Dishoeck & Black (1986)), of C_3 = 2×10^{-9}, C_4 $\leq 4\times10^{-9}$ to 10^{-10}, and C_5 $\leq 2\times10^{-10}$. The results of the two diffuse cloud models to which we have access yield abundances which are too high for C_3 by about an order of magnitude, 3×10^{-8} (Terzieva & Herbst 1998), and 5×10^{-8} (Turner 2000). The values from the former model correspond to quasi steady state after 10^5 years and the latter are

for $A_V = 1$ and n= 500 cm^{-1} chosen with depletions which provide a good fit for essentially all molecular species in translucent clouds and for the majority of species in diffuse clouds. Similarly, the predicted abundances are also too high for the longer chains with relative values of C_3:C_4:C_5 of 5:3:8 from Terzieva & Herbst (1998), although Turner (2000) gives 25:2:1. So it appears that photodissociation rates have been underestimated (or other depletion mechanisms such as electron attachment or absorption on grains need to be included). The upper limit we have obtained of 0.1 to the C_5:C_3 ratio is consistent with the result of infrared detection of both these species in a circumstellar shell with a ratio of 0.09 (Bernath et al. 1989), suggesting that our measurements may have been close to actually detecting C_5.

The detection of polyatomic species containing carbon atoms in diffuse and translucent interstellar clouds indicate comparable column densities, not larger than about 10^{12} to 10^{13} cm^{-2}. This set comprises the detection of C_3 in the optical region (Maier et al. 2001) as well as of the rotational spectra of the polar species, C_2H, C_3H_2 (Lucas & Liszt 2000) as examples. So far among polyatomic species only H_3^+ has column densities in the diffuse medium exceeding 10^{14} cm^{-2} (McCall et al. 1998). The implication of this for the search of appropriate molecular systems which could correspond to the stronger, narrower DIBs, with typical equivalent widths of 0.1 A, is as follows. Assuming that the species would have oscillator strengths of electronic transitions (in the visible) in the 1-10 range, as could be the case for carbon chains with 10-20 atoms, then the column density would have to be about 10^{11} to 10^{12} cm^{-2}. This column density could be easily attained by the larger carbon species, whatever their shape, because they are less efficiently photodissociated.

The suggestion by Douglas (1977) that long carbon chain molecules, C_n ($n = 5$-15) be considered as the carriers of DIBs, has now been tested directly for C_4 and C_5, showing that their abundance is too small. Thus the next step in attempting to identify carriers of the DIBs would be to obtain laboratory spectra of carbon species with 10-20 atoms having electronic transitions in the visible region (e.g., as is the case for C_{2n+1} n=8-20, Maier (1998)) and then making a direct comparison with astronomical observations at high S/N as has been demonstrated in this work.

Table 1.   The Observations of ζ Oph (HD 149757)

	3789 Å			5109 Å		K I Rad.Vel[d]
T[a]	S/N[b]	$W(10^{-4}\text{Å})^c$	T[a]	S/N[b]	$W(10^{-4}\text{Å})^c$	(km s^{-1})
11700	2300	0.67	10800	2600	0.50	-14.53 ± 0.18

[a]Total exposure times in seconds.

[b]per pixel

[c]3σ equivalent width detection limit for the band head (see section 2)

[d]from Maier et al. (2001)

REFERENCES

Baudrand J. & Vitry, R., 2000, Proc. SPIE, Astronomical Telescopes and Instrumentation 2000, in press.

Bernath, P.F., Hinkle, K.H., & Keady, J.J., 1989, Science, 244, 562.

Baudrand J. & Walker, G.A.H., 2001, PASP, 113, in press.

Crawford, I. A., 1997, MNRAS, 290, 41.

Douglas, A. E., 1977, Nature, 269, 130.

Forney, D., Freivogel, P., Grutter, M. & Maier, J. P., 1996, J. Chem. Phys., 104, 4954.

Freivogel, P., Grutter, M., Forney, D., & Maier, J.P., 1996, J. Chem. Phys.Lett., 249, 191.

Galazutdinov, G.A., Musaev, F.A., & Krełowski, J., 2001, MNRAS, 325, 1332.

Hanrath, M., & Peyerimhoff, S.D., 2001, J. Chem. Phys.Lett., 337, 368.

Herbig, G.H., 1995, ARA&A, 33, 19.

Kolbuszewski, M., 1995, J.Chem.Phys., 102, 3679.

Lambert, D.L., Sheffer, Y., Federman, S.R., 1995, ApJ, 438, 740.

Linnartz, H., Vaizert, O., Motyleweski, T., Maier, J.P., 2000, J. Chem. Phys., 112, 9777.

Lucas, R. & Liszt, H. S., 2000, A&A, 358, 1069.

Maier, J. P., 1998, J. Chem. Phys., 102, 3462.

Maier, J.P., Lakin, N.M., Walker, G.A.H., Bohlender, D.A., 2001, ApJ, 553, 267.

McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T., 1998, Science 279, 1910.

McCarthy,M.C., & Thaddeus,P., 2001, Chem.Soc.Rev., 30, 177.

Motylewski,T., Vaizert,O., Giesen,T.F., Linnartz,H., & Maier,J.P.,1999, J. Chem. Phys., 111, 6161.

Mühlhäuser,M., Froudakis, G.E., Hanrath,M., & Peyerimhoff, S.D., 2000, J. Chem. Phys.Lett., 324, 195.

Pacchioni,G., & Koutecky, J., 1988, J. Chem. Phys., 88, 1066.

Smith, W. H., Snow, T. P., York, D. G., 1977, ApJ, 218, 124.

Terzieva,R., & Herbst,E., 1998, ApJ., 501, 207.

Turner,B.E., 2000, ApJ, 542,837.

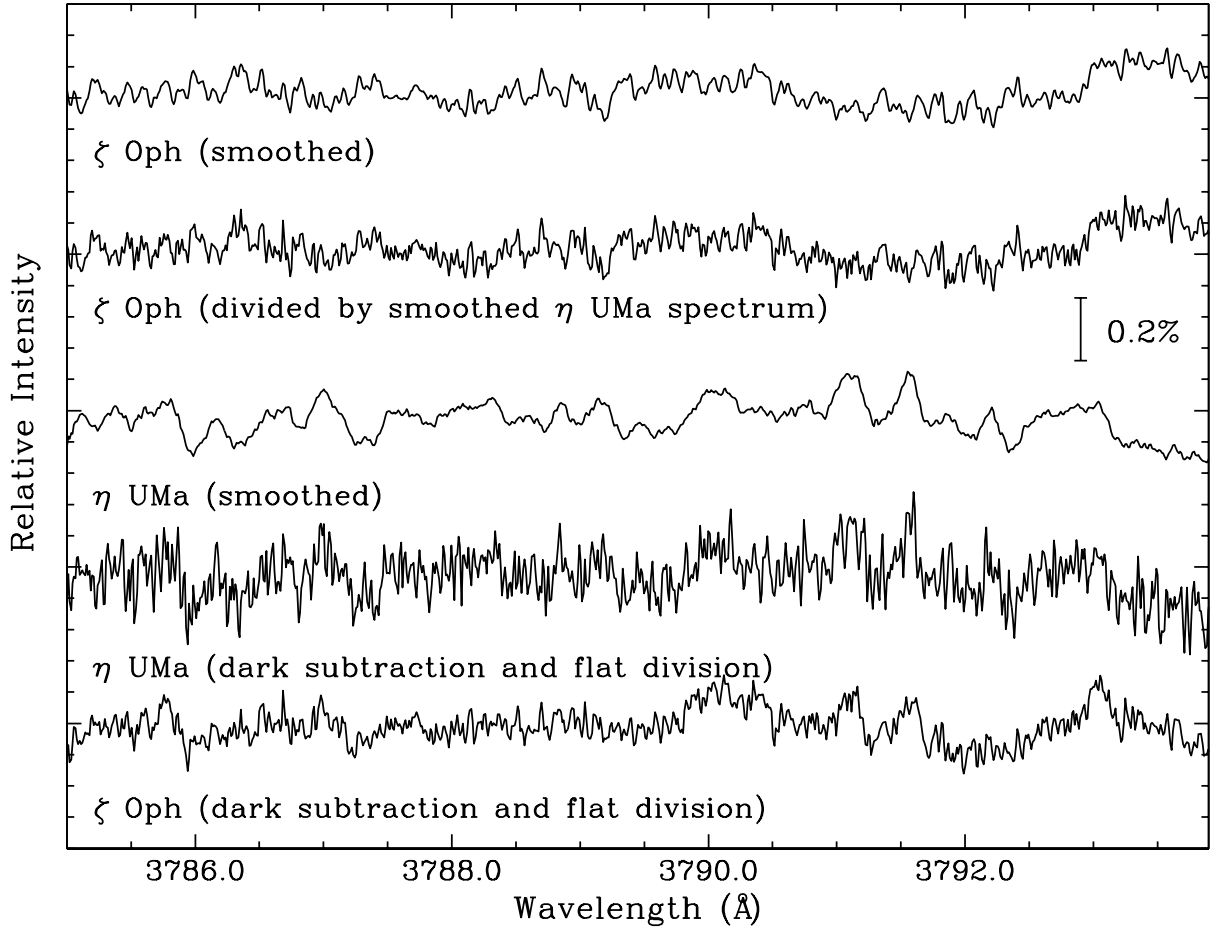van Dishoeck, E. F. & Black, J. H., 1986, ApJS, 62, 109.

Fig. 1.— The final reduction sequence for the spectra at 3790 Å. The flat field spectra contained a coarse structure absent from the stellar spectra which can be seen as common residuals in the dark subtracted and flat-fielded spectra for ζ Oph and η UMa in the two bottom plots. The processed spectra of η UMa were smoothed and then divided into the processed spectra of ζ Oph thereby largely removing the flat-field structure. The final 3-point smoothed spectrum of ζ Oph, the one discussed in the paper, is shown in the top plot.
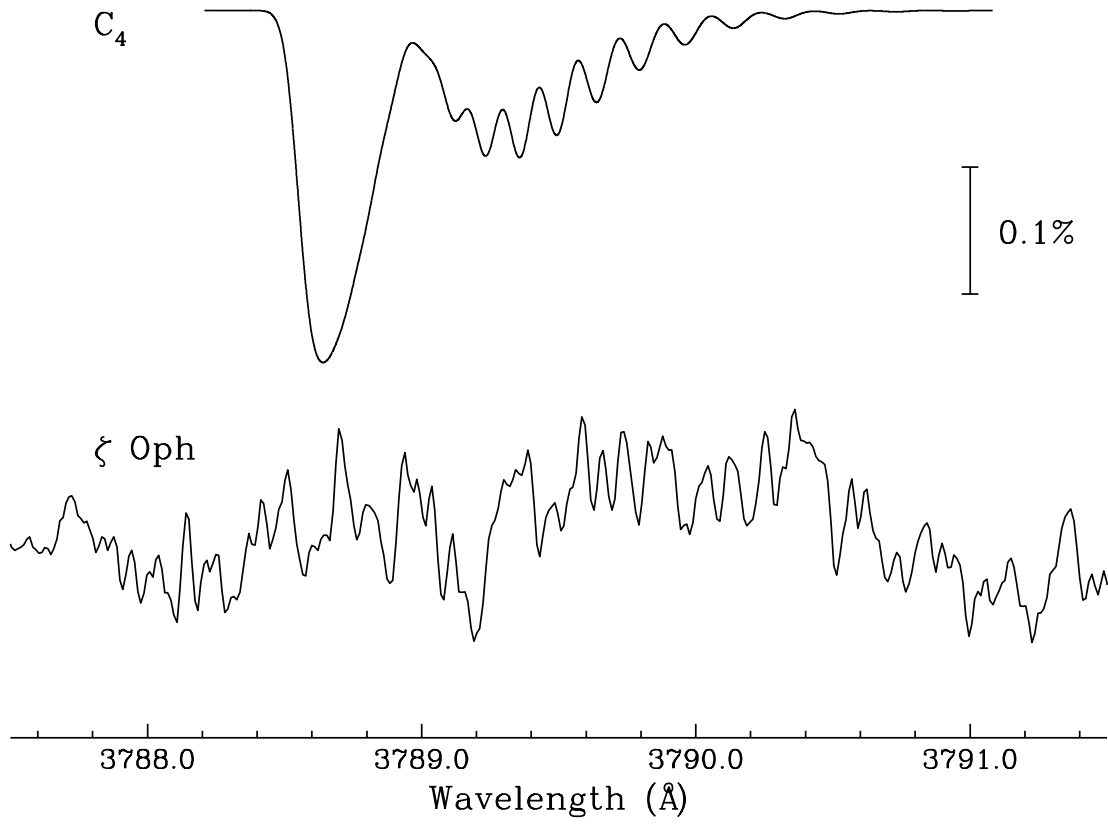
Fig. 2.— Comparison of a laboratory spectrum (top) of C$_4$ at 3788 Å from Linnartz et al. (2000) smoothed to a spectral resolution of 110,000 and compared to the observed spectrum (lower) of ζ Oph from Figure 1.
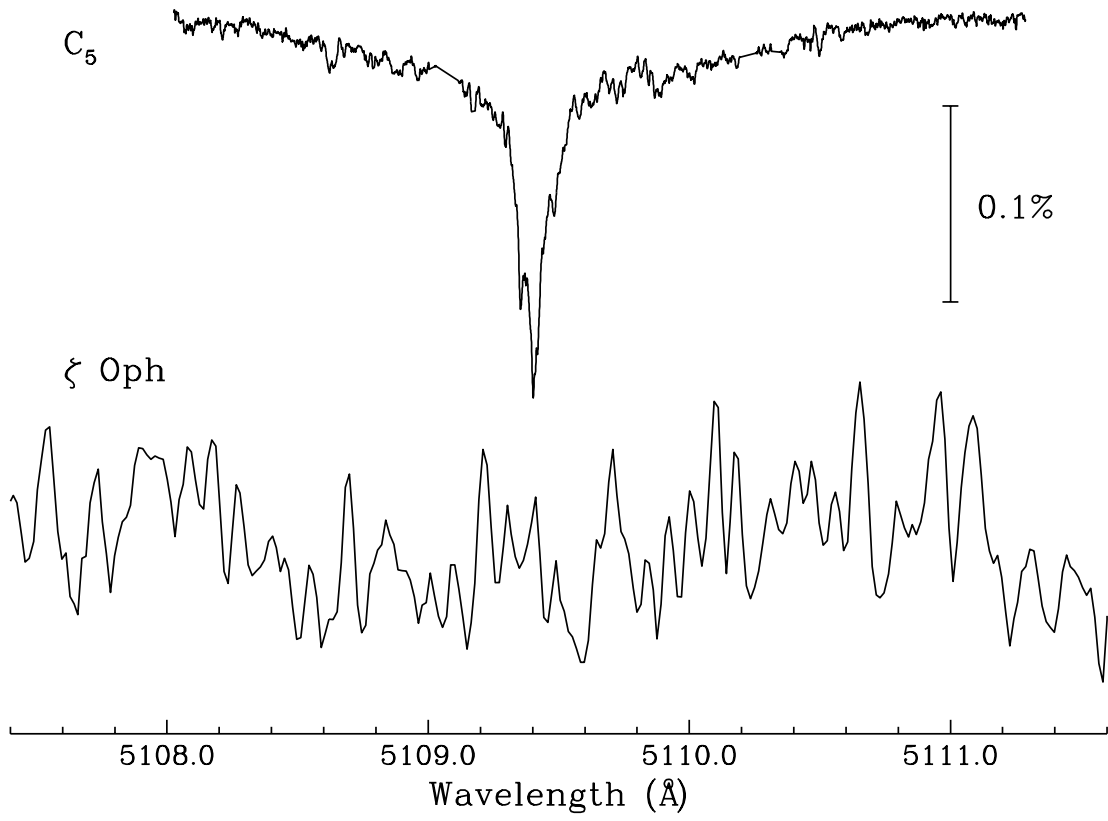
Fig. 3.— Comparison of a laboratory spectrum (top) of C_5 at 5109 Å from Motylewski et al. (1999) smoothed to a spectral resolution of 110,000 and compared to the observed spectrum (lower) of ζ Oph.